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(54) Title: SUBSTITUTED CARBOXANILIDOTHIAZOLES AND THEIR USE AS FUNGICIDES

## (57) Abstract

The present invention relates to certain substituted 5-carboxanilidothiazoles and their use as fungicides.

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SUBSTITUTED CARBOXANILIDOTHIAZOLES  
AND THEIR USE AS FUNGICIDES

Field of the Invention

The present invention relates to certain  
5 substituted 5-carboxanilidothiazoles and their use  
as fungicides.

Background of the Invention

Various substituted carboxanilidothiazoles  
are known in the art as fungicides. A known fungicide,  
10 2-amino-4-methyl-5-(carboxyanilido)thiazole, is sold  
under the trademark Seedvax. However, there still is  
a need in the art for fungicides which have the  
advantages of being safe on crops and efficacious at  
low application rates for cost savings and lower  
15 pesticide load on the environment.

Summary of the Invention

The present invention relates to certain  
substituted 5-carboxanilidothiazoles and their use in  
the control of plant fungus diseases such as, for  
20 example Basidiomycetes. The carboxanilidothiazoles of  
the present invention are substituted on the thiazole  
ring as follows (the sulfur atom being the 1-position):  
in the 2-position on the thiazole ring - a halo  
substituent preferably chloro, bromo or iodo and most  
25 preferably a chloro substituent; (ii) in the  
4-position of the thiazole ring - a dihalomethyl or  
trihalomethyl, preferably trihalomethyl, most  
preferably trifluoromethyl, and (iii) in the  
5-position of the thiazole ring - a carboxanilido  
30 substituent uniquely having at least three electron  
withdrawing substituents on the phenyl ring. The  
electron withdrawing substituents are selected from

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halo, (preferably chloro, iodo or bromo),  $C_{1-2}$  haloalkyl (preferably perhaloalkyl, preferably trifluoromethyl),  $C_{1-2}$  haloalkoxy (preferably halomethoxy, preferably trifluoromethoxy),  $C_{1-2}$  5 alkoxy, cyano and nitro. Preferred electron withdrawing groups are chloro, bromo, iodo,  $C_{1-2}$  perhaloalkyl and halomethoxy. When there are only three electron withdrawing substituents on the phenyl ring, the substituents are located in the ortho and 10 para positions. Preferably the para substituent, if any, also has lipophilic character.

The open positions on the phenyl ring of the carboxanilido group may also be substituted by a variety of other substituents other than hydrido which 15 do not unacceptably interfere with the fungicidal activity of the molecule. Such substituents are preferably in the meta position. Suitable substituents include lower alkyl, lower alkylthio, lower alkylcarbonyl, lower alkoxy carbonyl and the 20 like. Other types of suitable substituents will be known to those skilled in the art.

The degree of substitution on the phenyl ring of the carboxanilido group will vary from 3 to 5 but unstable molecules such as those with trinitro 25 substitution or tetra or penta iodo substitution are outside the scope of this invention. The compounds of the present invention have good fungicidal activity at low application rates such as, for example on Basidiomycetes and are generally safe to the host 30 plant. A more thorough disclosure of the present invention is presented in detailed description which follows.

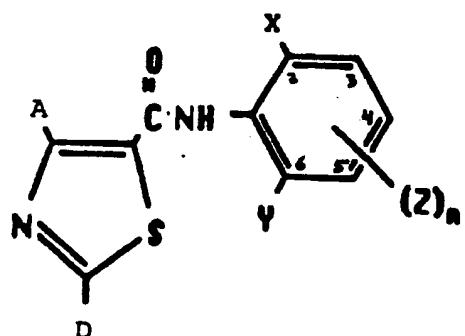
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Detailed Description

The present invention relates to certain substituted 5-carboxanilidothiazoles, compositions thereof and their use in the control of plant fungus disease such as, for example Basidiomycetes such as Rhizoctonia, Sclerotium and Corticum and other fungi such as Botrytis, Colletotrichum, Fusarium, Gaeumannomyces, and Sclerotium.

A preferred embodiment of the unique class of 5-carboxanilidothiazoles of the present invention are compounds represented by the Formula I and agronomically acceptable salts thereof:

Formula I



wherein A is dihalomethyl or trihalomethyl; D is halo; X is halo, C<sub>1-2</sub> haloalkyl, C<sub>1-2</sub> alkoxy, C<sub>1-2</sub> haloalkoxy, cyano or nitro; Y is chloro, bromo, iodo, C<sub>1-2</sub> perhaloalkyl, dihalomethoxy or trihalomethoxy; each Z is independently halo, C<sub>1-2</sub> haloalkyl, or C<sub>1-2</sub> haloalkoxy and n is an integer from 1 to 3 provided that when n is 1, Z is in the 4-position. Preferably A is trihalomethyl, most preferably trifluoromethyl. Preferably D is chloro. Preferably X and Z as C<sub>1-2</sub> haloalkyl or C<sub>1-2</sub> haloalkoxy have at least two halo substituents and more preferably 3 or more halo substituents. Preferably, X, Y and Z are each

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independently chloro, bromo, iodo,  $C_{1-2}$  perhaloalkyl (preferably trifluoromethyl) or trihalomethoxy (preferably trifluoromethoxy).

The term "carboxanilido" means  $C_6H_5NHCO-$ .

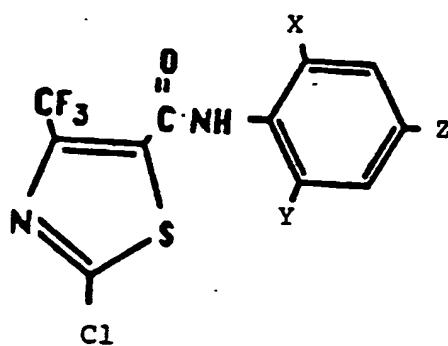
5 The term "halo" means fluoro, chloro, bromo or iodo.

The term "lower alkyl" means  $C_{1-5}$  alkyl.

Open positions on the phenyl ring of Formula I which do not have a Z substituent may be substituted 10 by other substituents which either enhance the activity of the molecule or do not unacceptably hinder the activity. Molecules having such substituents are contemplated as equivalents of the compounds claimed herein. Such substituents include the electronegative 15 substituents described herein or substituents such as lower alkylthio, lower alkyl, lower alkoxy, lower alkylcarbonyl or lower alkoxy carbonyl. Those skilled in the art will be able to select other types of suitable substituents.

20 Another preferred embodiment of the unique class of 5-carboxanilidothiazoles of the present invention are compounds represented by the Formula II and agronomically acceptable salts thereof:

Formula II



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wherein X is halo, trihalomethyl, trihalomethoxy, nitro or cyano; Y and Z are independently chloro, bromo, iodo, trihalomethyl (preferably trifluoromethyl) dihalomethoxy (preferably difluoromethoxy) or trihalomethoxy (preferably trifluoromethoxy).

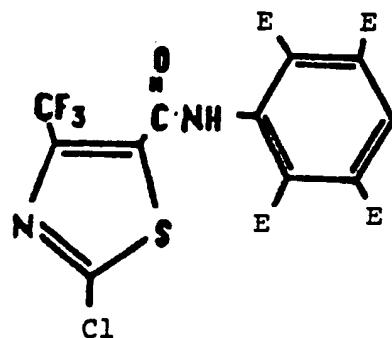
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Open positions on the phenyl ring of Formula II may be substituted by other substituents which either enhance the activity of the molecule or do not unacceptably hinder the activity such as electro-  
10 negative substituents as described herein or substituent such as lower alkyl, lower alkoxy, lower alkylthio, lower alkylcarbonyl, or lower alkoxy- carbonyl. Compounds having such substituents are contemplated as equivalents of the compounds claimed  
15 herein.

Another preferred embodiment of the unique class of 5-carboxanilidothiazoles of the present invention are compounds represented by the Formula III and agronomically acceptable salts thereof:

20

Formula III



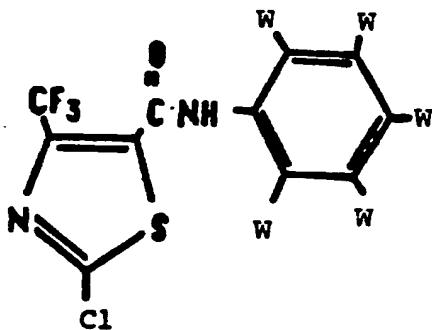
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wherein each E is independently chloro, bromo, iodo, trifluoromethyl or trifluoromethoxy.

The open position on the phenyl ring of Formula III may be substituted by other substituents which either enhance the activity of the molecule or do not unacceptably hinder the activity such as electronegative substituents as described herein or a substituents such as lower alkyl, lower alkoxy, lower alkylthio, lower alkylcarbonyl or lower alkoxy carbonyl. Compounds having such substituents are contemplated as equivalents of the compounds claimed herein.

Another preferred embodiment of the unique class of 5-carboxanilidothiazoles of the present invention are compounds represented by the Formula IV and agronomically acceptable salts thereof:

Formula IV



wherein each W is independently chloro, bromo, iodo, trifluoromethyl or trifluoromethoxy. W is preferably chloro.

Agronomically acceptable salts of the present invention include alkali, alkaline earth, acid addition, base addition and alkylation salts.

Other suitable electron withdrawing ring substituents for compounds of the present invention include pentahalosulfur, preferably pentafluorosulfur, halomethylthio, haloethylthio, (C<sub>1-2</sub> alkyl or C<sub>1-2</sub> haloalkyl) sulfinyl or (C<sub>1-2</sub> alkyl or C<sub>1-2</sub> haloalkyl) sulfonyl. Compounds having such electron withdrawing substituents on the phenyl ring in accordance with the present invention are contemplated as equivalents of the compounds claimed herein.

The procedures described below depict suitable methods whereby the compounds of this invention may be prepared by known chemical procedures from compounds which are known in the art and/or are readily available commercially. These procedures described below are merely illustrative and those skilled in the art will know a variety of other procedures suitable for use in making the compounds of the present invention.

Compounds of the present invention can be prepared by reacting an appropriately substituted thiazole having a 5-carbonylchloride substituent with an appropriately substituted aniline in suitable solvent(s) at an elevated temperature. Suitable solvents include xylene, THF, toluene, chlorobenzene, collidine, and 2,6-di-t-butyl-4-methyl pyridine. In some cases, acid acceptors such as tertiary amines and pyridines may be used to accelerate the rate of reaction. The acid acceptor may also function as the solvent.

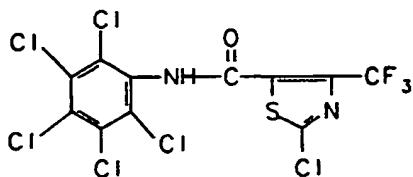
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Appropriately substituted anilines are commercially available or may be prepared by standard chemical procedures. For example, halo substituted anilines can be prepared by halogenation of 5 appropriately substituted anilines using standard techniques.

The thiazoles are conveniently prepared by the following sequential reactions: (i) reacting ethyl 4,4,4 trifluoro-2-chloroacetoacetate with 10 thiourea in a suitable solvent, preferably DMF to form ethyl 2-amino-4-trifluoromethyl-5-thiazole-carboxylate; (ii) reacting the product of (i) with HCl and sodium nitrite (or with amyl nitrite and cuprous chloride) to from 2-chloro-4-trifluoromethyl- 15 5-thiazolecarboxylate and (iii) converting the product of (ii) into the corresponding acid chloride with sequential hydrolysis with base and reaction with thionyl chloride.

The following Examples 1-5 are detailed 20 descriptions of methods of preparation of certain compounds of the present invention. These detailed preparations fall within the scope of, and serve to exemplify, the more generally described methods of preparation set forth above. These Examples are 25 presented for illustrative purposes only and are not intended as a restriction on the scope of the invention.

Example 1



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2-chloro-4-trifluoromethyl-5-(pentachlorocarboxanilido) thiazole.

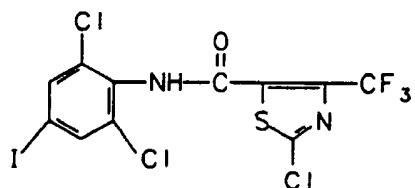
To a solution of 5.31 g (0.02 mol) of pentachloroaniline in 50 ml of xylene was added 5.0 g (0.02 mol) of 2-chloro-4-trifluoromethyl-5-chlorocarbonyl thiazole and the resulting solution heated to reflux for 4 days. The mixture was cooled and petroleum ether added to precipitate a white solid. The solid was purified on TLC in 30:70 ethylacetate: hexane to give 5.14 g of a solid m.p. 237-238°C.

Elemental Analysis for  $C_{11}HN_2SCl_6OF_3$

	<u>C</u>	<u>H</u>	<u>N</u>
Calculated:	27.59	0.21	5.85
Found:	27.68	0.37	6.01

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Example 2



2-chloro-4-trifluoromethyl-5-(2',6'-dichloro-4-iodo-carboxanilido) thiazole.

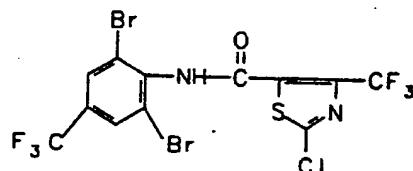
To a solution of 2.9 g (0.01 mol) of 2',6'-dichloro-4-iodoaniline was added 2.5 g (0.01 mol) of 2-chloro-4-trifluoromethyl-5-chlorocarbonyl thiazole and the mixture heated to reflux for 12 hours. The mixture was cooled to room temperature and cyclohexane was added to precipitate 3.1 g of a white crystalline product m.p. 200-202°C (yield 62%).

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Elemental Analysis for  $C_{11}H_3Cl_3F_3IN_2OS$ 

	<u>C</u>	<u>H</u>	<u>N</u>
Calculated:	26.34	0.6	5.59
Found:	25.89	0.64	5.47

5

Example 3

2-chloro-4-trifluoromethyl-5-(2',6'-dibromo-4-trifluoromethyl carboxanilido) thiazole.

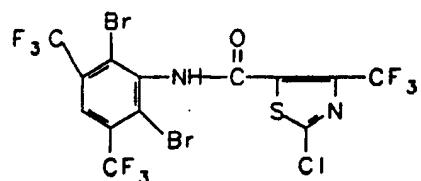
To the solution of 3.2 g (0.01 mol) of 2',6'-bromo-4-trifluoromethylaniline was added 2.5 g (0.01 mol) of 2-chloro-4-trifluoromethyl-5-chloro-carbonyl thiazole and 70 ml of xylene and the mixture heated to reflux for 18 hours. The mixture was cooled to room temperature, evaporated to low volume and cyclohexane was added to precipitate 2.8 g of a white crystalline product m.p. 178-180°C (yield 53%).

Elemental Analysis for  $C_{12}H_3ClBR_2F_6N_2OS$ 

	<u>C</u>	<u>H</u>	<u>N</u>
Calculated:	27.07	0.57	5.26
Found:	28.13	0.83	5.19

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Example 4



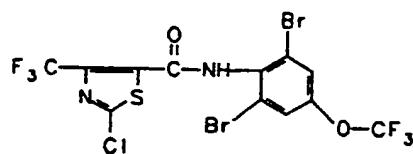
2-chloro-4-trifluoromethyl-5-(2',6'-dibromo-3',5'-di[trifluoromethyl]carboxanilido) thiazole.

2.33 g (0.005 mol) of 2',6'-dibromo-3',5'-di[trifluoromethyl]aniline was mixed with 1.5 g (0.006 mol) of 2-chloro-4-trifluoromethyl-5-chlorocarbonyl thiazole and 1.44 g (0.007 mol) of 2,6-di-tertbutyl-2-methyl pyridine and heated at 120°C for 3 hours. The mixture was cooled to room temperature, dissolved in ethyl acetate and water and transferred to a separation funnel. Sodium bicarbonate was added and the organic layer separated, dried and evaporated until crystals formed. Heptane was added and the crystals collected to give 1.81 g of a white crystalline solid m.p. 226-227.

Elemental Analysis

	<u>C</u>	<u>H</u>
Calculated:	26.0	0.34
Found:	26.05	0.41

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Example 5

2-chloro-4-trifluoromethyl-5-(2',6'-dibromo-4-trifluoromethoxy carboxanilido) thiazole.

To the solution of 3.35g (0.01 mol) of 2',6'-dibromo-4-trifluoromethoxyaniline was added 2.5g (0.01 mol) of 2-chloro-4-trifluoromethyl-5-chlorocarbonyl thiazole and 70 ml of toluene and the mixture heated to reflux for 18 hours. The mixture was cooled to room temperature, evaporated to low volume and cyclohexane was added to precipitate 4.2g of a white crystalline product m.p. 138-140°C (yield 76%).

Elemental Analysis for  $C_{12}H_3Br_2ClF_6N_2O_2S$

	<u>C</u>	<u>H</u>	<u>N</u>
Calculated:	26.28	0.55	5.11
15      Found:	27.8	0.93	4.97

Using procedures similar to those set out in detail above, further compounds of the present invention were prepared and are shown in the following Table I.

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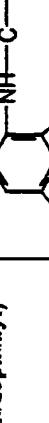
TABLE I

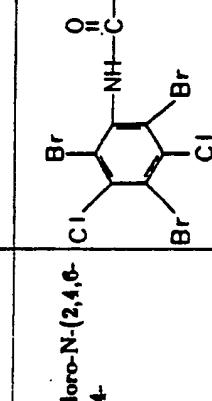
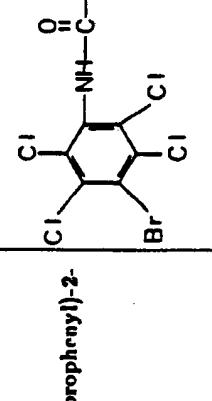
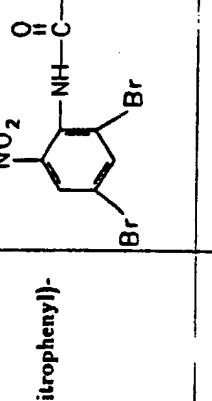
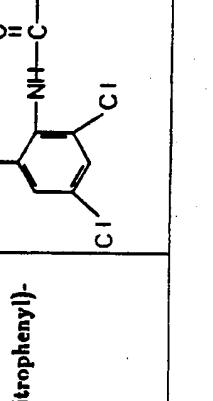
Example Compound #	Name	Structure	Analysis (%)		
			Calcd	Found	
<b>6</b>	5-thiaolecarboxamide, 2-chloro-N-[2,4-dibromo-6-(trifluoromethyl)phenyl]-4-(trifluoromethyl)-		C 27.07 H 0.57 Br 30.01 Cl 6.66 F 21.41 N 5.26 S 6.02	C 26.75 H 0.75 Br 30.01 Cl 6.66 F 21.41 N 5.17 S 6.02	
<b>7</b>	5-thiaolecarboxamide, 2-chloro-N-[2,4,6-trichlorophenyl]-4-(trifluoromethyl)-		C 32.22 H 0.74 Cl 34.59 F 13.90 N 6.83 S 7.82	C 32.41 H 0.79 Cl 34.59 F 13.90 N 6.83 S 7.82	
<b>8</b>	5-thiaolecarboxamide, 2-chloro-N-[2,4,6-tribromophenyl]-4-(trifluoromethyl)-		C 24.31 H 0.56 Br 44.12 Cl 6.52 F 10.49 N 5.16 S 5.90	C 24.46 H 0.61 Br 44.12 Cl 6.52 F 10.49 N 5.16 S 5.90	
<b>9</b>	5-thiaolecarboxamide, N-(4-bromo-2-chloro-4-dichlorophenyl)-2-chloro-4-(trifluoromethyl)-		C 29.07 H 0.67 Br 17.58 Cl 23.40 F 12.54 N 6.16 S 7.05	C 28.65 H 0.83 Br 17.58 Cl 23.40 F 12.54 N 6.09 S 7.05	

Example Compound #	Name	Structure	Analysis (%)		
			Calc'd	Found	
10	5-thiaolecarboxamide, 2-chloro-N-(2,4-dibromo-6-chlorophenyl)-4-(trifluoromethyl)-		C 26.48 H 0.61 Br 32.03 Cl 14.21 F 11.42 N 5.61 S 0.43	C 26.73 H 0.59 Br 32.03 Cl 14.21 F 11.42 N 5.61 S 0.43	
11	5-thiaolecarboxamide, N-(2-bromo-4,6-dichlorophenyl)-2-chloro-4-(trifluoromethyl)-		C 29.07 H 0.67 Br 17.58 Cl 23.40 F 12.54 N 6.16 S 7.05	C 29.07 H 0.67 Br 17.58 Cl 23.40 F 12.54 N 6.16 S 7.05	
12	5-thiaolecarboxamide, N-(4-chloro-2,6-dibromophenyl)-2-chloro-4-(trifluoromethyl)-		C 26.48 H 0.61 Br 32.03 Cl 14.21 F 11.42 N 5.61 S 0.43	C 26.48 H 0.61 Br 32.03 Cl 14.21 F 11.42 N 5.61 S 0.43	
13	5-thiaolecarboxamide, N-[2-bromo-6-nitro-4-(trifluoromethyl)-phenyl]-2-chloro-4-(trifluoromethyl)-		C 28.91 H 0.61 Br 16.03 Cl 7.11 F 22.86 N 8.43 S 0.43	C 28.86 H 0.61 Br 16.03 Cl 7.11 F 22.86 N 8.43 S 0.43	

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Example Compound #	Name	Structure	Analysis (%) Calc'd Found
14	5-thiaolecarboxamide, 2-chloro-N-[2-chloro-6-nitro-4-(trifluoromethyl)phenyl]-4-(trifluoromethyl)-		C 31.74 31.76 H 0.67 0.68 Cl 15.61 F 25.10 N 9.25 9.22 S 7.06
15	5-thiaolecarboxamide, N-(2-bromo-4,6-difluorophenyl)-2-chloro-4-(trifluoromethyl)-		C 31.34 31.71 H 0.72 0.78 Br 18.95 Cl 8.41 F 22.53 N 6.64 6.71 S 7.61
16	5-thiaolecarboxamide, N-(2-bromo-6-chloro-4-fluorophenyl)-2-chloro-4-(trifluoromethyl)-		C 30.16 30.24 H 0.69 0.73 Br 18.24 Cl 16.19 F 17.35 N 6.40 6.41 S 7.32
17	5-thiaolecarboxamide, 2-chloro-N-(2,6-dibromo-4-iodophenyl)-4-(trifluoromethyl)-		C 22.38 24.07 H 0.51 0.66 Br 27.07 Cl 6.00 F 9.65 I 21.49 N 4.74 5.03 S 5.43

Example Compound #	Name	Structure	Analysis (%) Calc'd Found
18	5-thiaolecarboxamide, 2-chloro-N-(2,4-dichloro-6-indophenyl)-4-(trifluoromethyl)-		C 28.35 28.67 H 0.60 0.77 Cl 21.21 F 11.37 I 25.31 N 5.59 5.61 S 0.39
19	5-thiaolecarboxamide, 2-chloro-N-(2,6-dibromo-3-chloro-4-fluorophenyl)-4-(trifluoromethyl)-		C 25.56 25.66 H 0.39 0.61 Br 30.92 Cl 13.72 F 14.70 N 5.42 5.41 S 0.20
20	5-thiaolecarboxamide, 2-chloro-N-(2,3,5,6-tetrachlorophenyl)-4-(trifluoromethyl)-		C 29.72 29.77 H 0.45 0.48 Cl 39.88 F 12.82 N 6.30 S 7.21
21	5-thiaolecarboxamide, 2-chloro-N-[2,4-dibromo-6-(2,2,2-trifluoroethoxy)phenyl]-4-(trifluoromethyl)-		C 27.76 27.63 H 0.90 0.92 Br 28.41 Cl 6.30 F 20.27 N 4.98 5.00 S 5.70

Example Compound #	Name	Structure	Analysis (%) Calc'd Found
22	5-thiaolecarboxamide, 2-chloro-N-(2,4,6-tribromo-3,5-chlorophenyl)-4-(trifluoromethyl)-		C 21.58 21.55 H 0.16 0.32 Br 39.15 Cl 17.37 CF <sub>3</sub> S 9.31 F 4.56 N 4.56 Cl 5.24 S 5.24
23	5-thiaolecarboxamide, -N-(4-bromo-2,3,5,6-tetrachlorophenyl)-2-chloro-4-(trifluoromethyl)-		C 25.24 24.63 H 0.19 0.38 Br 15.27 Cl 33.87 CF <sub>3</sub> S 10.89 N 5.35 5.24 Cl 6.13 S 6.13
24	5-thiaolecarboxamide, -2-chloro-N-(2,4-dibromo-6-nitrophenyl)-4-(trifluoromethyl)-		C 25.93 25.66 H 0.59 0.61 Br 31.37 Cl 6.96 CF <sub>3</sub> F 11.19 N 8.25 8.18 S 6.29
25	5-thiaolecarboxamide, -2-chloro-N-(2,4-dichloro-6-nitrophenyl)-4-(trifluoromethyl)-		C 31.41 31.45 H 0.72 0.74 Cl 25.29 CF <sub>3</sub> F 13.55 N 9.99 S 7.62

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Example Compound #	Name	Structure	Analysis (%) Calc'd Found
26	5-thiaolecarboxamide, N-(2-bromo-4-fluoro-2-nitrophenyl)-2- chloro-4-(trifluoromethyl)-		C 29.45 29.29 H 0.67 0.92 Br 17.61 Cl 7.90 F 16.94 N 9.37 9.27 S 7.15
27	5-thiaolecarboxamide, N-(2-bromo-4-chloro-6-nitrophenyl)-2- chloro-4-(trifluoromethyl)-		C 28.41 28.39 H 0.65 0.63 Br 17.16 Cl 15.25 F 12.26 N 9.04 9.06 S 6.89
28	5-thiaolecarboxamide, 2-chloro-N-(4- dibromo-2-cyano-3-fluorophenyl)-4- (trifluoromethyl)-		C 28.40 28.48 H 0.40 0.44 Br 31.49 Cl 6.99 F 14.98 N 8.28 8.21 S 6.52
29	5-thiaolecarboxamide, 2-chloro-N-[2,6- dibromo-4-(2,2,2-trifluoroethoxy)phenyl]- 4-(trifluoromethyl)-		C 27.76 28.26 H 0.90 0.82 Br 28.41 Cl 6.30 F 20.27 N 4.98 4.89 S 5.70

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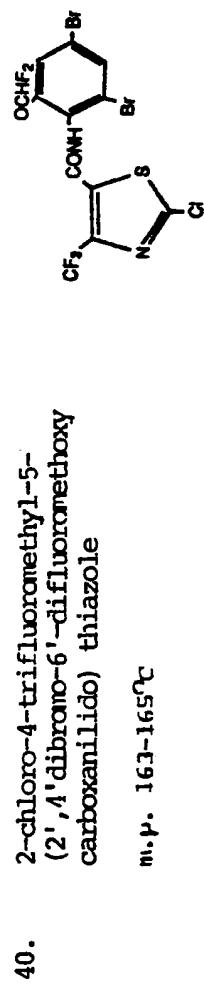
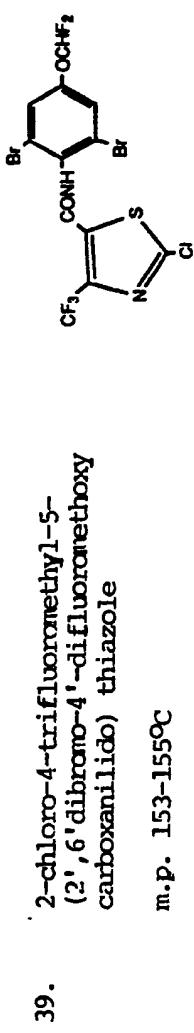
Example Compound #	Name	Structure	Analysis (%) Calc'd Found
<b>30</b>	5-thiaolecarboxamide, 2-chloro-N-(2,3,4,5-tetrachloro-6-methoxyphenyl)-		C 30.38 30.39 H 0.85 0.89 Cl 37.36 F 12.01 N 5.90 S 6.76
<b>31</b>	5-thiaolecarboxamide, 2-chloro-N-(2,4,6-tribromo-3-nitrophenyl)-4-(trifluoromethyl)-		C 22.45 22.46 H 0.34 0.50 Br 40.74 Cl 6.03 F 9.69 N 7.14 7.15 S 5.45
<b>32</b>	5-thiaolecarboxamide, 2-chloro-N-(2,4,6-tribromo-3-cyanophenyl)-4-(trifluoromethyl)-		C 25.36 25.52 H 0.35 0.62 Br 42.17 Cl 6.24 F 10.03 N 7.39 7.19 S 5.64
<b>33</b>	5-thiaolecarboxamide, N-(3-acetyl-2,4,6-tribromophenyl)-2-chloro-4-(trifluoromethyl)-		C 26.67 26.74 H 0.86 0.81 Br 40.95 Cl 6.06 F 9.74 N 4.79 4.75 S 5.46

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Example Compound #	Name	Structure	Analysis (%)		
			Calc'd	Found	
34	benzoic acid, 2,4,6-tribromo-3-[[2-chloro-4-(trifluoromethyl)-5-thiisoxolyl]carbonyl]amino], methyl ester MP: 178.0-179.0		C 25.96 H 0.84 Br 39.86 Cl 5.89 F 9.48 N 4.66 S 5.33	C 26.04 H 0.89 Br 39.86 Cl 5.89 F 9.48 N 4.66 S 5.33	
35	5-thiaolecarboxamide, 2-chloro-N-(2,4,6-tribromo-3,5-dimethylphenyl)-4-(trifluoromethyl)- MP: 206.0-208.0		C 27.32 H 1.23 Br 41.95 Cl 6.20 F 9.97 N 4.90 S 5.01	C 27.20 H 1.26 Br 41.95 Cl 6.20 F 9.97 N 4.85 S 5.01	
36	5-thiaolecarboxamide, 2-chloro-N-(2,4,6-tribromo-3-methoxyphenyl)-4-(trifluoromethyl)- MP: 218.0-220.0		C 25.14 H 0.88 Br 41.81 Cl 6.16 F 9.94 N 4.84 S 5.59	C 25.63 H 0.88 Br 41.81 Cl 6.16 F 9.94 N 4.84 S 5.59	
37	5-thiaolecarboxamide, 2-chloro-N-[2,6-dibromo-4-chloro-3-(trifluoromethyl)-phenyl]-4-(trifluoromethyl)- MP: 165.0-197.0		C 25.42 H 0.36 Br 26.19 Cl 12.51 F 20.11 N 4.94 S 5.66	C 25.31 H 0.48 Br 26.19 Cl 12.51 F 20.11 N 4.94 S 5.66	

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Example Compound #	Name	Structure	Analysis (%)		
			Calcd	Found	
36	5-thiaolecarboxamide, 2-chloro-N-(2,4-dibromo-6-cyanophenyl)- 4-(trifluoromethyl)-		C 29.44 H 0.62 Br 33.65 CF <sub>3</sub> 7.24 Cl 11.64 N 8.58 S 0.55	29.33 0.64 33.65 Cl 7.24 F 11.64 N 8.58 S 0.55	



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Primary Test For  
Activity On Rice Sheath Blight

5       The Rhizoctonia solani is cultured on rice grain inoculum at room temperature in darkness in the laboratory. Inoculum is prepared by mixing one part rice grain, one part chopped rice grain and one part water. The mixture is autoclaved twice before use. Sclerotia of the fungus are added to each flask and the inoculum is ready for use when mycelia of  
10       Rhizoctonia solani have ramified throughout the medium and new sclerotia have formed (generally in about four to eight weeks).

15       Rice plant seeds, 16-18, are planted in the center of a 3 inch square pot ( $7.62 \text{ cm}^2$ ) and covered with steam sterilized soil (silt loam, rediearth and osmocote). The pots are placed in the greenhouse at 25-30°C, with 14 hours of lighting. In about 11-15 days the plants are in the second to third leaf stage and ready for testing.

20       The test compounds are diluted to 1% by weight solution in acetone. Prior to application, the test solutions are prepared in concentrations of 0.5; 0.1 and 0.02mg/ml having a formulation of 40% acetone, 0.4% Tween-20 and 59.6% water.

25       Plants are sprayed at the second to third leaf stage. Two ml of the formulation is drenched onto the soil of the pot, approximately 1.5 ml/pot is then foliarly applied using a "Devilbiss 152" atomizer. The atomizer is rinsed with acetone between  
30       treatments.

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The rice plants are allowed to air dry at room temperature before being returned to the greenhouse. The pots are placed into a specially fabricated plastic flood tray. There are no drain holes in the trays, so water is retained in the system.

All pots are kept in the flood trays, which are filled with water to the soil line before inoculation. Two days later, approximately 2 grams of the inoculum is applied to each pot at the base of the clump of rice. The trays are then placed into a dark growth room at 100% relative humidity and 25 C. After at least 24 hours of darkness, the lights are turned onto a 12 hour light cycle. The plants are left undisturbed for 4 to 7 days and then rated for disease control. Disease control is assessed on the presence and severity of Sheath Blight lesions as compared to control pots. One rating for each treatment (four pots) is taken.

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The following rating scale is used:

0 = No activity  
1 = Low activity  
2 = Moderate activity  
5  
3 = High activity

Table II summarizes the results of tests conducted to determine the fungicidal activity of the compounds of this invention.

TABLE II

10	<u>Example</u>	<u>Concentration of Test Soln(mg/ml)</u>	<u>Activity Rating</u>
	1	0.5/0.1/0.02	3/3/2
	2	0.5/0.1/0.05	3/3*/2*
	3	0.5/0.1/0.05	2/2.5*/2
15	4	0.5/0.1/0.02	3/3*/3
	5	0.5/0.1/0.02	3/3/3
	6	0.5/0.1/0.05	3/3/3
	7	0.5/0.1	3/0
	8	0.5/0.1/0.02	3/2.3*/0
20	9	0.5/0.1/0.05	3/0.5*/0
	10	0.5/0.1/0.05	3/1.5*/1
	11	0.5/0.1	3/1
	12	0.5/0.1	3/0
	13	0.5	**

25 \* average of 2 or more test replications  
\*\* plant injury

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TABLE II Continued

<u>Example</u>	<u>Concentration of Test Soln(mg/ml)</u>	<u>Activity Rating</u>
5	14	0.1/0.02
	15	0.5/0.1
	16	0.5/0.1
	17	0.5/0.1/0.05
	18	0.5/0.1/0.05
	19	0.5/0.1/0.02
10	20	0.5/0.1
	21	0.5/0.1
	22	0.5/0.1/0.05
	23	0.5/0.1/0.05
	24	0.5/0.1/0.05
	25	0.1/0.05
15	26	0.5/0.1
	27	0.1/0.05
	28	0.1/0.02
	29	0.5/0.1/0.02
	30	0.5/0.1/0.05
	31	0.5/0.1
20	32	0.5/0.1/0.05
	33	0.5/0.1/0.02
	34	0.5/0.1/0.02
	35	0.5/0.1
	36	0.5/0.1
	37	0.5/0.1/0.05
25	38	0.5
	39	0.5/0.1/0.02
	40	0.5/0.1/0.02
		3/3/1

\*\* plant injury

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Advanced Testing For  
Activity On Rice Sheath Blight

The host seeds are planted and *R. solani* is  
cultured as previously described. The plants are  
5 inoculated at the three leaf stage. To inoculate the  
plants, the inoculum is removed from the flasks,  
broken into small bits or individual grains and a  
small amount (1 cm<sup>3</sup>) is added to the base of each  
clump of rice plants. After inoculation, the plants  
10 are moved to a dark growth room set for fog and 25C.  
Lights are returned to a 12 hour day/night cycle after  
24 hours of darkness.

The test solutions are prepared in the same  
manner as in the primary test.

15 For foliar application, the plants are  
sprayed when the third leaf is fully expanded but the  
fourth leaf has not emerged. The surface of all pots  
is covered with a layer of vermiculite before chemical  
application which is removed immediately after appli-  
20 cation for all foliar spray tests. Compounds are  
applied using a DeVilbiss air-brush sprayer. Two  
ml/pot volume is applied which is enough to cover all  
surfaces of the plants to wetness but not enough to  
cause the material to drip from the leaves. Plants  
25 are moved to the drying room after spraying (very low  
light conditions) and after 3-4 hours are moved to the  
greenhouse bench. If plants are planted on day "0",  
then typically the chemical is applied on day 14, and  
pathogen inoculation occurs on day 16. Evaluation of  
30 disease will be made on day 26 to 30. Disease is  
evaluated by estimating the amount of stem tissue that

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is covered by symptoms; water soaking, chlorosis and necrosis and converted to a percent control as compared to the formulation treated check.

5       The protocol for the soil drench protective test is identical to that of the foliar protectant test except for the method of applying the chemical. Chemical test solutions are prepared and are applied to the soil surface with a pipette (1ml/pot). Plants are moved to the greenhouse within 30 minutes of  
10      treatment. Plants are watered immediately with sufficient water to fill the top of the pot and kept for 2 days with the soil saturated. Inoculation, incubation and evaluation are made on the same schedule and in the same manner as the foliar  
15      protectant test.

Table III summarizes the results of tests conducted to determine the fungicidal activity of the compounds of this invention.

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TABLE III

<u>Example</u>	<u>Test</u>	<u>Concentration of Test Solution*</u>	<u>% of Control</u>
5	1	Foliar	0.1
			92+
			0.05
			86+
			0.02
			68+
	Soil	0.01	50+
10	2	Foliar	0.20
			78+
15	3	Foliar	0.04
			32+
20	4	Foliar	0.05
			68
25	5	Foliar	0.02
			63
30	6	Foliar	0.05
			56
30	7	Foliar	0.02
			86
30	8	Foliar	0.1
			100
			0.02
			100
30	8	Soil	1.0
			100
			0.2
			85
30	8		0.04
			35
			0.1
			96
30	8		0.05
			72
			0.02
			99
30	8		0.01
			36
			0.05
			83
30	8		0.02
			64
			0.1
			89
30	8		0.05
			14
			0.02
			25
30	8		0.01
			8
			0.05
			63+
30	8		0.02
			95
30	8		0.01
			17

\* Foliar is mg/ml - soil drench is mg/pot

+ Average of 2 or more tests

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TABLE III  
Continued

<u>Example</u>	<u>Test</u>	<u>Concentration Of Test Solution *</u>	<u>% of Control</u>
5	9	0.05	59
		0.02	36
10	10	0.05	59
		0.02	40
10	11	0.05	42
		0.02	42
15	12	0.05	31
		0.02	15
15	13	0.05	93
		0.02	95
15	17	0.05	94
		0.02	80
20	18	0.05	77
		0.02	55
20	19	0.5	97
		0.1	92
		0.02	78
25	20	0.05	80
		0.02	81
25	22	0.05	100
		0.02	85
25	23	0.05	100
		0.02	97
25	24	0.05	74
		0.02	52

30      \* Foliar is mg/ml - soil drench is mg/pot

      + average of 2 or more tests

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TABLE III  
Continued

<u>Example</u>	<u>Test</u>	<u>Concentration Of Test Solution*</u>	<u>% of Control</u>
5	25	0.05	57
		0.02	29
10	30	0.05	53
		0.02	51
15	31	0.05	41
		0.02	36
		0.1	100
		0.05	85+
		0.02	100
20	32	0.01	37+
		1.0	100
		0.2	38
		0.04	58
25	33	0.05	100
		0.02	83
		0.5	99
30	34	0.1	89
		0.02	10
		0.2	40
37	35	0.04	7
		0.1	99
		0.05	67
		0.02	40
38	36	0.1	96
		0.05	99
		0.02	85+
30	38	0.05	93
		0.02	66

\* Foliar is mg/ml - soil drench is mg/pot

+ Average of 2 or more tests

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Test For Activity On Brown Patch

Creeping bentgrass was grown in greenhouse in five inch diameter plastic pots for a period of 6 weeks. One day prior to test initiation the turf 5 was mowed to approximately one inch in height. The test compounds were formulated as flowables. The formulated materials were dissolved in appropriate amount of water to give final test 10 solutions having concentrations of 1, 0.2 and 0.04 mg/ml of active ingredient.

Four pots or replicates were used for each treatment with each test pot receiving 5 ml of test solution. Treatments were applied to turf foliage using DeVilbiss type sprayer. Pots were placed in 15 growth chamber at 28C, 95% humidity and 12 hours lighting at 400 uE/meter square.

The test pathogen Rhizoctonia solani was cultured on sterilized sorghum seed three weeks prior to test initiation. Two days after chemical treatment pots 20 were inoculated by placing ten Rhizoctonia infested sorghum seed in each pot. Inoculated pots were returned to growth chamber and daylength was reduced to 8 hours to encourage Rhizoctonia infestation and brown patch symptoms.

25 Ten days after inoculation, test pots were removed from growth chamber and evaluated for disease and phytotoxicity. The percent Rhizoctonia brown patch infection was evaluated in each pot.

The test results are shown in Table IV.

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TABLE IV

<u>COMPOUND FROM EXAMPLE</u>	<u>CONCENTRATION OF TEST SOLUTION (mg/ml)</u>	<u>% CONTROL</u>
5	1	91
1	0.2	92
1	0.04	22

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Test For Activity on Peanut White Mold

Peanuts are grown in the field on a 36 inch row spacing using normal agronomic practices. Individual plots consisted of two adjacent rows cut into 5 50 foot length for a total of 100 row feet per plot. The test compounds were formulated as flowables and applied at rates which varied the amount of active ingredient per acre. Rates were calculated on a broadcast basis while the test solutions were applied 10 in a 12 inch band centered over the plant row. Spray volume was 25 gallons/A (238 l/hA) and the test solutions were applied through even flat fan nozzle tips. Four replicate plots are used for each treatment. The test plots received three applications, one 15 at pegging, one 4 weeks after pegging and one 8 weeks after pegging. The test pathogen Sclerotium rolfsii was cultured on sterilized oat seed for 21 days. The fungus/oat seed mixture was removed from culture flasks, air dried for 3 days, and then stored at room 20 temperature until use (within 30 days). At approximately 70 days after planting, 250 ml of the fungus/oat seed inoculum was applied to each plot by dispersing the inoculum mixture down the center of both plot rows. The artificial inoculum was used as a 25 supplement to the natural pathogen population present at the test site. Test treatments were evaluated for disease and phytotoxicity by counting total disease loci in the treated plot rows. A disease locus was one dead plant or up to 12 linear inches of row with 30 dead plants. Evaluations were made at 130 days after planting. The test results are shown in Table V.

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TABLE V

<u>Example</u>	<u>Application Rate (oz/A)</u>	<u>% Control</u>
1	8 (226.4)*	69
5 1	16 (452.8)*	94
1	32 (905.6)*	97

\* (gram/A)

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As can be seen from the data above, the  
compounds of the present invention have good  
fungicidal activity at low application rates for  
resulting cost savings and lower pesticide load on the  
5 environment. The compounds of the present invention  
generally exhibit good fungicide control generally  
with no plant injury or with transient plant injury.

10 The fungicidal compositions of this  
invention, including concentrates which require  
dilution prior to application, contain at least  
one active ingredient and an adjuvant in liquid or  
solid form. The compositions are prepared by admixing  
the active ingredient with an adjuvant including  
diluents, extenders, carriers, and conditioning agents  
15 to provide compositions in the form of finely-divided  
particulate solids, granules, pellets, solutions,  
dispersions or emulsions. Thus, it is believed that  
the active ingredient could be used with an adjuvant  
such as a finely-divided solid, a liquid of organic  
20 origin, water, a wetting agent, a dispersing agent, an  
emulsifying agent or any suitable combination of  
these.

25 Suitable wetting agents are believed to  
include alkyl benzene and alkyl naphthalene sulfon-  
ates, sulfated fatty alcohols, amines or acid amides,  
long chain acid esters of sodium isothionate, esters  
of sodium sulfosuccinate, sulfated or sulfonated fatty  
acid esters, petroleum sulfonates, sulfonated  
vegetable oils, ditertiary acetylenic glycols,  
30 polyoxyethylene derivatives of alkylphenols (partic-  
ularly isooctylphenol and nonylphenol) and poly-  
oxyethylene derivatives of the mono-higher fatty  
acid esters of hexitol anhydrides (e.g., sorbitan).

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Suitable dispersants are methyl, cellulose, polyvinyl alcohol, sodium lignin sulfonates, polymeric alkyl naphthalene sulfonates, sodium naphthalene sulfonate, polymethylene bisnaphthalene sulfonate and poly-  
5 ethyleneoxide-polypropyleneoxide copolymers.

Wettable powders are water-dispersible compositions containing one or more active ingredients, an inert solid extender and one or more wetting and dispersing agents. The inert solid  
10 extenders are usually of mineral origin such as the natural clays, diatomaceous earth and synthetic minerals derived from silica and the like. Examples of such extenders include kaolinites, attapulgite clay and synthetic magnesium silicate. The wettable powders  
15 compositions of this invention usually contain from above 0.5 to 60 parts (preferably from 5-20 parts) of active ingredient, from about 0.25 to 25 parts (preferably 1-15 parts) of wetting agent, from about 0.25 to 25 parts (preferably 1.0-15 parts) of  
20 dispersant and from 5 to about 95 parts (preferably 5-50 parts) of inert solid extender, all parts being by weight of the total composition. Where required, from about 0.1 to 2.0 parts of the solid inert extender can be replaced by a corrosion inhibitor or  
25 anti-foaming agent or both.

Other formulations include dust concentrates comprising from 0.1 to 60% by weight of the active ingredient on a suitable extender; these dusts may be diluted for application at concentrations within the  
30 range of from about 0.1-10% by weight.

Aqueous suspensions or emulsions may be prepared by stirring a nonaqueous solution of a water-insoluble active ingredient and an emulsification agent

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with water until uniform and then homogenizing to give stable emulsion of very finely-divided particles.

The resulting concentrated aqueous suspension is characterized by its extremely small particle size, so that when diluted and sprayed, coverage is very uniform. Suitable concentrations of these formulations contain from about 0.1-60% preferably 5-50% by weight of active ingredient, the upper limit being determined by the solubility limit of active ingredient in the solvent.

Concentrates are usually solutions of active ingredient in water-immiscible or partially water-immiscible solvents together with a surface active agent. Suitable solvents for the active ingredient of this invention include dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone, hydrocarbons, and water-immiscible ethers, esters, or ketones. However, other high strength liquid concentrates may be formulated by dissolving the active ingredient in a solvent then diluting, e.g., with kerosene, to spray concentration.

The concentrate compositions herein generally contain from about 0.1 to 95 parts (preferably 5-60 parts) active ingredient, about 0.25 to 50 parts (preferably 1-25 parts) surface active agent and where required about 4 to 94 parts solvent, all parts being by weight based on the total weight of emulsifiable oil.

Granules are physically stable particulate compositions comprising active ingredient adhering to or distributed through a basic matrix of an inert, finely-divided particulate extender. In order to aid leaching of the active ingredient from the particulate extender, a surface active agent such as those listed hereinbefore can be present in the composition.

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Natural clays, pyrophyllites, illite, and vermiculite are examples of operable classes of particulate mineral extenders. The preferred extenders are the porous, absorptive, preformed particles such as 5 preformed and screened particulate attapulgite or heat expanded, particulate vermiculite and the finely-divided clays such as kaolin clays, hydrated attapulgite or bentonitic clays. These extenders are sprayed or blended with the active ingredient to form 10 the herbicidal granules.

The granular compositions of this invention may contain from about 0.1 to about 30 parts by weight of active ingredient per 100 parts by weight of clay and 0 to about 5 parts by weight of surface active 15 agent per 100 parts by weight of particulate clay.

Suitable types of formulations are emulsifiable concentrates, flowables, wettable powders, dusts and granules. A suitable flowable formulaion (3lb/gal) (0.35 kg/l) is as follows:

	<u>INGREDIENTS</u>	<u>% BY WGT</u>
20	Compound of Example 1	31.14
	Xanthan gum	1.25
	block copolymers of	
	propylene oxide and	
25	ethylene oxide	2.50
	magnesium aluminum	
	silicate	1.00
	lignosulfonate dispersant	2.00
	defoamer	0.25
30	water	<u>61.86</u>
		100.00

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The compounds of the present invention generally appear to show the greatest activity when applied as a foliar spray.

The compositions of this invention can also 5 contain other additaments, for example, other fungicides, fertilizers, insecticides, herbicides, other pesticides, safeners and the like used as adjuvants or in combination with any of the above described adjuvants. Other fungicides can be useful 10 in combination with the active ingredients of this invention including fungicides having activity on Rhizoctonia. Fungicides which may be useful in combination with compounds of the present invention include:

15	Tricyclazole	propiconazole
	Pyroquilon	prochloraz
	Chlorothalonil	maneb/mancozeb
	Triadimenol	Iprodione
	Fenpropimorph	Thiabendazole
20	Carbendazim	Probeuazole
	Triadimefon	Edifenphos
	Flusilazol	IBP
	Metalaxyl	Isoprothiolane

Other suitable fungicides will be known to 25 those skilled in the art.

When operating in accordance with the present invention, effective amounts of the compounds of this invention are applied to the foliage or vegetative propagules or may be incorporated into the soil or 30 water around the foliage in any convenient fashion. The application of liquid and particulate solid compositions to the soil can be carried out by conventional

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methods, e.g., power dusters, boom and hand sprayers and spray dusters. The compositions can also be applied from airplanes as a dust or a spray because of their effectiveness at low dosages.

5           The exact amount of active ingredient to be employed is dependent upon various factors, including the plant species and stage of development of plants and disease, the type and condition of soil, the amount of rainfall and the specific compounds employed.

10          In selective foliar application a dosage of from about 30 to about 500 g/ha preferably from about 60 to about 250 g/ha, is usually employed. In soil applications a dosage of from about 100 to about 1000 g/ha, preferably from about 250 to about 500 g/ha is usually

15          employed. Lower or higher rates may be required in some instances. One skilled in the art can readily determine from this specification, including the above examples, the optimum rate to be applied in any particular case.

20          Although the invention is described with respect to specific modifications, the details thereof are not to be construed as limitations, for it will be apparent that various embodiments, changes and modifications may be resorted to without departing from the spirit and scope thereof and it is understood that such equivalent embodiments are intended to be included within the scope of this invention.

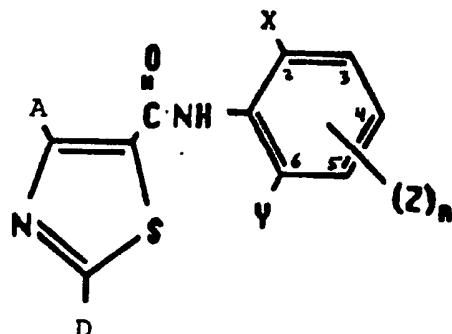
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WE CLAIM:

1. A compound selected from those represented by the Formula I and agronomically acceptable salts thereof:

5

Formula I

wherein A is dihalomethyl or trihalomethyl; D is halo; X is halo, C<sub>1-2</sub> haloalkyl, C<sub>1-2</sub> alkoxy, C<sub>1-2</sub> haloalkoxy, cyano or nitro; Y is chloro, bromo, iodo, C<sub>1-2</sub> perhaloalkyl, dihalomethoxy or trihalomethoxy; 10 each Z is independently halo, C<sub>1-2</sub> haloalkyl, or C<sub>1-2</sub> haloalkoxy; and n is an integer from 1 to 3; provided that when n is 1, Z is in the 4-position.

2. The compound of claim 1 wherein D is chloro.

15 3. The compound of claim 2 wherein A is trihalomethyl.

4. The compound of claim 3 wherein A is trifluoromethyl.

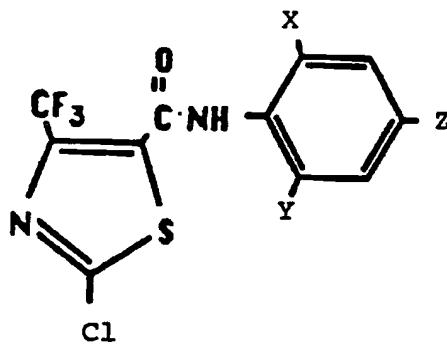
20 5. The compound of claim 4 wherein X, Y and Z are each independently chloro, bromo, iodo, C<sub>1-2</sub> perhaloalkyl or trihalomethoxy.

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6. The compound of claim 5 wherein X, Y and Z are each independently chloro, bromo, iodo, trifluoromethyl or trifluoromethoxy.

5 7. A compound selected from those represented by the Formula II and agronomically acceptable salts thereof:

Formula II

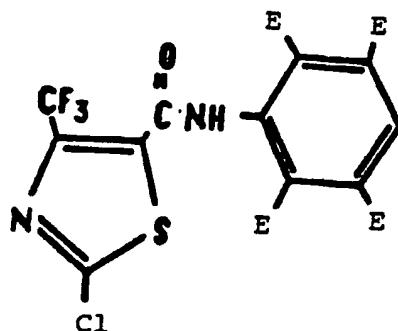


10 wherein X is halo, trihalomethyl, trihalomethoxy, nitro or cyano; Y and Z are independently chloro, bromo, iodo, trihalomethyl or trihalomethoxy.

8. The compound of claim 7 wherein Y and Z are independently chloro, bromo, iodo, trifluoromethyl or trifluoromethoxy.

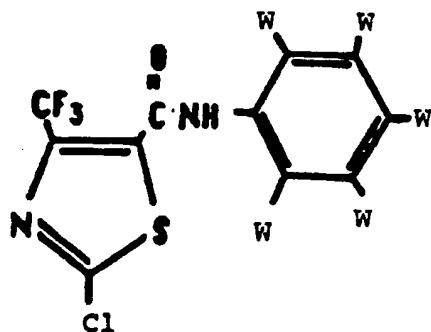
15 9. A compound selected from those represented by the Formula III and agronomically acceptable salts thereof:

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Formula III

wherein each E is independently chloro, bromo, iodo, trifluoromethyl or trifluoromethoxy.

10. A compound selected from those  
5 represented by the Formula IV and agronomically  
acceptable salts thereof:

Formula IV

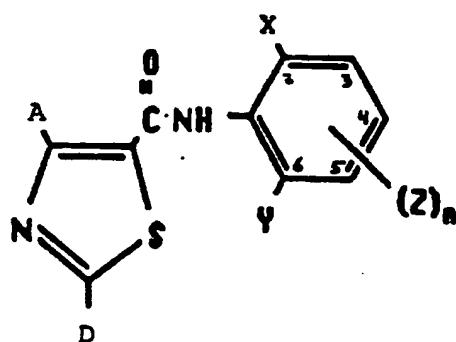
wherein each W is independently chloro, bromo, iodo, trifluoromethyl or trifluoromethoxy.

10 11. A compound of Claim 10 wherein W is  
chloro.

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12. A fungicidal composition comprising a fungicidally effective amount of a compound selected from those represented by the Formula I and agro-nomically acceptable salts thereof:

5

Formula I

10

wherein A is dihalomethyl or trihalomethyl; D is halo; X is halo, C<sub>1-2</sub> haloalkyl, C<sub>1-2</sub> alkoxy, C<sub>1-2</sub> haloalkoxy, cyano or nitro; Y is chloro, bromo, iodo, C<sub>1-2</sub> perhaloalkyl, dihalomethoxy or trihalomethoxy; each Z is independently halo, C<sub>1-2</sub> haloalkyl, or C<sub>1-2</sub> haloalkoxy; and n is an integer from 1 to 3; provided that when n is 1, Z is in the 4-position.

13. The composition of claim 12 wherein D is chloro.

15

14. The composition of claim 13 wherein A is trihalomethyl.

15. The composition of claim 14 wherein A is trifluoromethyl.

20

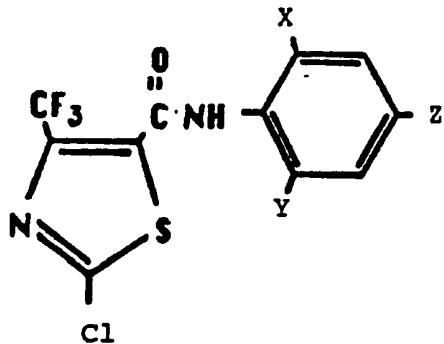
16. The composition of claim 15 wherein X, Y and Z are each independently chloro, bromo, iodo, C<sub>1-2</sub> perhaloalkyl or trihalomethoxy.

-45-

17. The composition of claim 16 wherein X, Y and Z are each independently chloro, bromo, iodo, trifluoromethyl or trifluoromethoxy.

5 18. A fungicidal composition comprising a fungidically effective amount of a compound selected from those represented by the Formula II and agro-nomically acceptable salts thereof:

Formula II

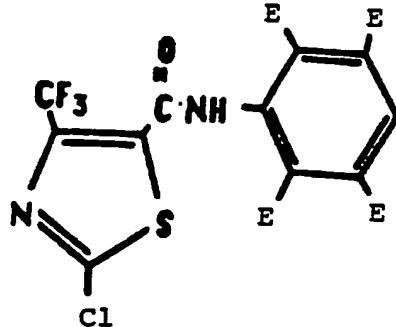


10 wherein X is halo, trihalomethyl, trihalomethoxy, nitro or cyano; Y and Z are independently chloro, bromo, iodo, trifluoromethyl or trifluoromethoxy.

19. The composition of claim 18 wherein Y and Z are independently chloro, bromo, iodo, trifluoromethyl or trifluoromethoxy.

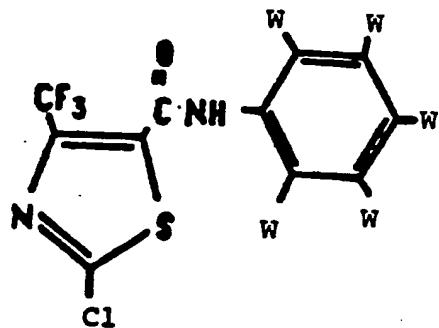
15 20. A fungicidal composition comprising a fungidically effective amount of a compound selected from those represented by the Formula III and agro-nomically acceptable salts thereof:

-46-

Formula III

wherein each E is independently chloro, bromo, iodo, trifluoromethyl or trifluoromethoxy.

21. A fungicidal composition comprising a fungidically effective amount of a compound selected from those represented by the Formula IV and agronomically acceptable salts thereof:

Formula IV

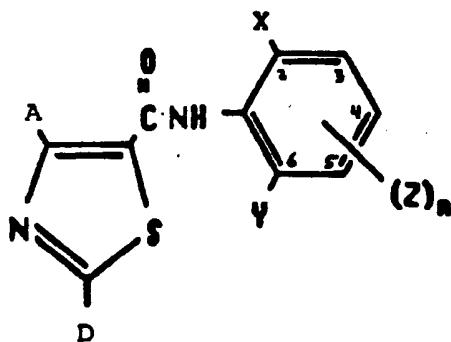
wherein each W is independently chloro, bromo, iodo, trifluoromethyl or trifluoromethoxy.

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22. The composition of Claim 21 wherein W is chloro.

23. A method of controlling the growth of fungus disease on a plant comprising applying to the 5 plant locus an effective amount of a compound selected from those represented by the Formula I and agro-nomically acceptable salts thereof:

Formula I



wherein A is dihalomethyl or trihalomethyl; D is 10 halo; X is halo, C<sub>1-2</sub> haloalkyl, C<sub>1-2</sub> alkoxy, C<sub>1-2</sub> haloalkoxy, cyano or nitro; Y is chloro, bromo, iodo, C<sub>1-2</sub> perhaloalkyl, dihalomethoxy or trihalomethoxy; each Z is independently halo, C<sub>1-2</sub> haloalkyl, or C<sub>1-2</sub> haloalkoxy; and n is an integer from 1 to 3; 15 provided that when n is 1, Z is in the 4-position.

24. The method of claim 23 wherein D is chloro.

25. The method of claim 24 wherein A is trihalomethyl.

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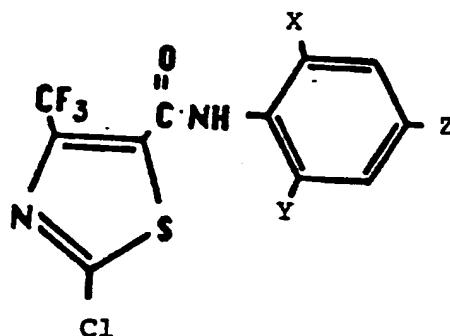
26. The method of claim 25 wherein A is trifluoromethyl.

27. The method of claim 26 wherein X, Y and Z are each independently chloro, bromo, iodo, 5 C<sub>1-2</sub> perhaloalkyl or trihalomethoxy.

28. The method of claim 27 wherein X, Y and Z are each independently chloro, bromo, iodo, trifluoromethyl or trifluoromethoxy.

29. A method of controlling the growth of 10 fungus disease on a plant comprising applying to the plant locus an effective amount of a compound selected from those represented by the Formula II and agro-nomically acceptable salts thereof:

Formula II



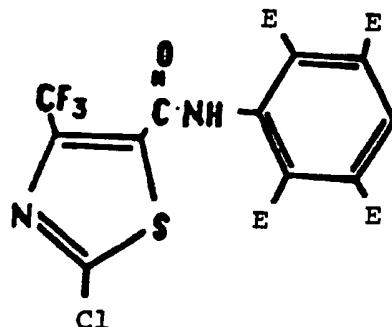
15 wherein X is halo, trihalomethyl, trihalomethoxy, nitro or cyano; Y and Z are independently chloro, bromo, iodo, trihalomethyl or trihalomethoxy.

20 30. The method of claim 29 wherein Y and Z are independently chloro, bromo, iodo, trifluoromethyl or trifluoromethoxy.

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31. A method of controlling the growth of  
 fungus disease on a plant comprising applying to the  
 plant locus an effective amount of a compound selected  
 from those represented by the Formula III and agro-  
 nomically acceptable salts thereof:

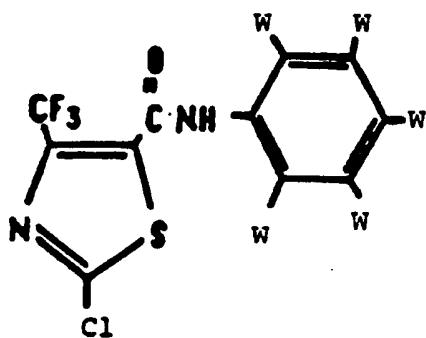
Formula III



wherein each E is independently chloro, bromo, iodo,  
 trifluoromethyl or trifluoromethoxy.

32. A method of controlling the growth of  
 10 fungus disease on a plant comprising applying to the  
 plant locus an effective amount of a compound selected  
 from those represented by the Formula IV and agro-  
 nomically acceptable salts thereof:

Formula IV



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wherein each W is independently chloro, bromo, iodo, trifluoromethyl or trifluoromethoxy.

33. A method according to Claim 32 wherein W is chloro.

## INTERNATIONAL SEARCH REPORT

PCT/US 90/04002

International Application No.

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC<sup>5</sup>: C 07 D 277/56, A 01 N 43/78

## II. FIELDS SEARCHED

Minimum Documentation Searched ?

Classification System	Classification Symbols
IPC <sup>5</sup>	C 07 D 277/00, A 01 N 43/00

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are included in the Fields Searched \*

## III. DOCUMENTS CONSIDERED TO BE RELEVANT \*

Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP, A, 0279239 (CIBA-GEIGY) 24 August 1988 see pages 1-2; page 19, example 3.075; claims 1,15,21-23 --	1-33
P,X	EP, A, 0335831 (CIBA-GEIGY) 4 October 1989 see pages 2-3; page 15, example 1.069 --	1-11
A	Chemical Abstracts, volume 81, no. 19, 11 November 1974, (Columbus, Ohio, US), M.F.A. Abdel-Lateef et al.: "Systemic and chemotherapeutic fungicidal activity-chemical structure relation of some 4-methyl-5-thiazolecarboxylic acid derivatives. Laboratory screening tests" see page 142, abstract no. 115750j & Acta Phytopathol. 1973, 8(3-4), 269-82 -----	1,12

\* Special categories of cited documents: <sup>10</sup>

"A" document defining the general state of the art which is not

considered to be of particular relevance

"E" earlier document but published on or after the international

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"L" document which may throw doubts on priority claim(s) or  
which is cited to establish the publication date of another  
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other means"P" document published prior to the international filing date but  
later than the priority date claimed"T" later document published after the international filing date  
or priority date and not in conflict with the application but  
cited to understand the principle or theory underlying the  
invention"X" document of particular relevance; the claimed invention  
cannot be considered novel or cannot be considered to  
involve an inventive step"Y" document of particular relevance; the claimed invention  
cannot be considered to involve an inventive step when the  
document is combined with one or more other such documents,  
such combination being obvious to a person skilled  
in the art

"A" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search  
10th October 1990

Date of Mailing of this International Search Report

08.11.90

International Searching Authority

Signature of Authorized Officer

EUROPEAN PATENT OFFICE

Mme N. KUIPER

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

US 9004002  
SA 38896

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 30/10/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A- 0279239	24-08-88	AU-A-	1097488	04-08-88
		JP-A-	63201178	19-08-88
EP-A- 0335831	04-10-89	AU-A-	3129189	21-09-89
		JP-A-	2015004	18-01-90

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